

ELECTROCHEMICAL OXIDATION OF FORMALDEHYDE ON THE PLATINUM ELECTRODE MODIFIED WITH LEAD AND COPPER ADATOMS

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ABSTRACT

Platinum electrodes prepared thermally were modified by lead and copper adatoms electrochemically. The prepared electrodes were characterized by a scanning electron microscope. The micrographs showed that the platinum surface is rough and porous. The electrochemical modification of the platinum surface by copper and lead adatoms is characterized by the presence of clusters of those metals on the platinum surface. The electrochemical measurements made in perchloric acid have shown that the presence of the lead or copper adatoms on the electrode surface decreases the charge linked to the adsorption or desorption of hydrogen atoms. The electrocatalytic performance of the platinum electrode for formaldehyde oxidation was improved with lead adatoms but not with copper adatoms. The result obtained with the platinum electrode modified by lead adatoms was interpreted as a bifunctional behaviour of the electrode towards formaldehyde oxidation. For the platinum electrode modified by the copper adatoms, the onset of the formaldehyde oxidation potential is almost similar to that of pure platinum. That was explained either by the inactivity of copper towards formaldehyde oxidation or by the detachment of the copper adatoms from the electrode surface exposing the platinum active sites for the organic compound oxidation.

Keywords : *lead, copper, adatom, formaldehyde, cyclic voltametry, adsorption.*

RÉSUMÉ

Oxydation électrochimique du formaldéhyde sur des électrodes de platine modifiées par les atomes de plomb et de cuivre

Les électrodes de platine préparées par voie thermique ont été modifiées électrochimiquement par des atomes de plomb et de cuivre. Les électrodes préparées ont été caractérisées par un microscope électronique à balayage. Les micro photos ont montré que la surface des électrodes de platine est rugueuse et poreuse. La modification de la surface du platine par les atomes de cuivre et de plomb est caractérisée par la présence d'agrégats de ces métaux sur la surface du platine. Les mesures électrochimiques faites dans l'acide perchlorique ont montré que la présence de plomb et de cuivre à la surface de l'électrode fait décroître la charge liée à l'adsorption et à la désorption de l'hydrogène. Le pouvoir électro catalytique de l'électrode de platine pour l'oxydation du formaldéhyde est amélioré en présence des atomes de plomb mais pas avec les atomes de cuivre. Le résultat obtenu avec le platine modifié par le plomb a été interprété comme un comportement bi fonctionnel de l'électrode vis-à-vis de l'oxydation du formaldéhyde. Pour l'électrode de platine modifiée avec les atomes de cuivre, le potentiel du début d'oxydation de formaldéhyde est presque similaire à celui observé sur le platine pur. Ceci a été expliqué soit par l'inactivité des atomes de cuivre vis-à-vis de l'oxydation du formaldéhyde soit par le détachement des atomes de cuivre de la surface de l'électrode exposant les sites actifs du platine à l'oxydation du composé organique.

Mots-clés : *plomb, cuivre, atome, formaldéhyde, voltammétrie cyclique, adsorption*

I – INTRODUCTION

Platinum electrodes were intensively used in many fields such as fuel cells [1-3] and wastewater treatments [4-6] due to their inertness characteristic and to their corrosion resistant properties. The platinum electrodes present remarkable electrocatalytic properties for organic compounds oxidation. Unfortunately, the electrocatalytic performances of the platinum electrode can decrease highly during such reactions. In the fuel cells domain where methanol is used as fuel, difficulties of its oxidation on the platinum happen. In fact, several studies [7] have shown that the oxidation of methanol on the platinum electrode led to the production of several adsorbed intermediates which block the platinum active sites. Among those intermediates there is the formaldehyde. That intermediate was known to be environmental unfriendly because of its high toxicity. Thus, in that work, formaldehyde will be used as

the organic matter and its oxidation will be realized on modified or unmodified platinum electrode. In order to solve the problem of the deactivation of platinum during organic compounds oxidation, some of the actual researches were focused on adding to platinum some metallic adatoms [5, 8-14] or some oxides [15]. Thus, several modified platinum catalysts such as Pt-Ru, Pt-Sn et Pt-Mo have been developed [16]. Even if those adatoms added to platinum contribute to increase its electrocatalytic activity for the oxidation of organic compounds etc... they are very expensive. In order to minimize the cost of the electrodes, the platinum electrode will be modified by abundant and low cost metals such as copper and lead which have been used as catalysts in several reactions [5, 17-22].

In the present work, several electrodes such as platinum, platinum modified by copper adatoms (Pt-Cu) and platinum modified by lead adatoms (Pt-Pb) will be prepared and then they will be characterized and applied for the oxidation of formaldehyde.

II – EXPERIMENTAL

The platinum coating precursor was prepared from H_2PtCl_6 (Fluka) dissolved in isopropanol (Fluka). The commercial products were used as received without any further treatment. The titanium substrate (1.6x1.6cmx0.5cm) was sandblasted to ensure good adhesion of the deposit on its surface. After, sandblasting, the substrate was washed vigourously in water and then in isopropanol to clean its surface from residual sands. The substrate was then dried in an oven at 80°C and weighted.

The precursor was applied by a painting procedure on the titanium (Ti) substrate then put in an oven for 15 min at 80 °C to allow the evaporation of the solvent. Then after, it is put in a furnace at 400 °C for 15 min to allow the decomposition of the precursor. Theses steps were repeated until the desired weight of the coating is reached. A final decomposition of 1 h was done at 400 °C.

The deposit morphology was analyzed with a Philips XL30 SFEG microscope operating at a field emission of 1-30kV.

The electrochemical measurements were performed in a three-electrode electrochemical cell using an Autolab PGStat 20 (Ecochemie). The counter electrode (CE) was a platinum wire and the reference electrode (RE) was a saturated calomel electrode (SCE). All the potential were converted against the standard hydrogen electrode (SHE). A luggin capillary was used to allow the reference electrode to be placed close to the working electrode (WE) by a distance of 1 mm. The apparent exposed surface area of the working

electrode was 1 cm². The experiments were made at ambient temperature (25°C).

The supporting electrolyte used was 1 M perchloric acid (HClO₄, Fluka). For the adatoms deposition, the solution of lead(II) nitrate (Fluka) and copper (II) sulfate (Fluka) were prepared and used. A solution of formaldehyde (Fluka) has also been used. All the solutions were made with distilled water.

III - RESULTS AND DISCUSSION

III-1. Morphologic aspect of the electrodes

All the microphotos present in *Figure 1* show that the surfaces of the coating layers are porous and rough. In photo A (*Figure 1*), one observes that the platinum grains are highly tightened between them. The same observation is made on photos B and C. The presence of the lead and the copper adatoms was characterized by the presence of clusters on the platinum surface.

III-2. Electrochemical investigations on the platinum electrodes in acidic electrolyte

Figure 2 presents the voltammogram of the freshly prepared platinum electrode in the perchloric acid (1M) electrolyte. Thirty cycles were made on that electrode in the whole domain of potential explored. There was no change in the voltammogram shape during the cycles. The first and the last (30th) voltammogram were perfectly superimposed. Those results indicated that the prepared electrode is stable. No significant charge increase due to hydration occurs as it is generally observed with thermally prepared oxide electrodes [23].

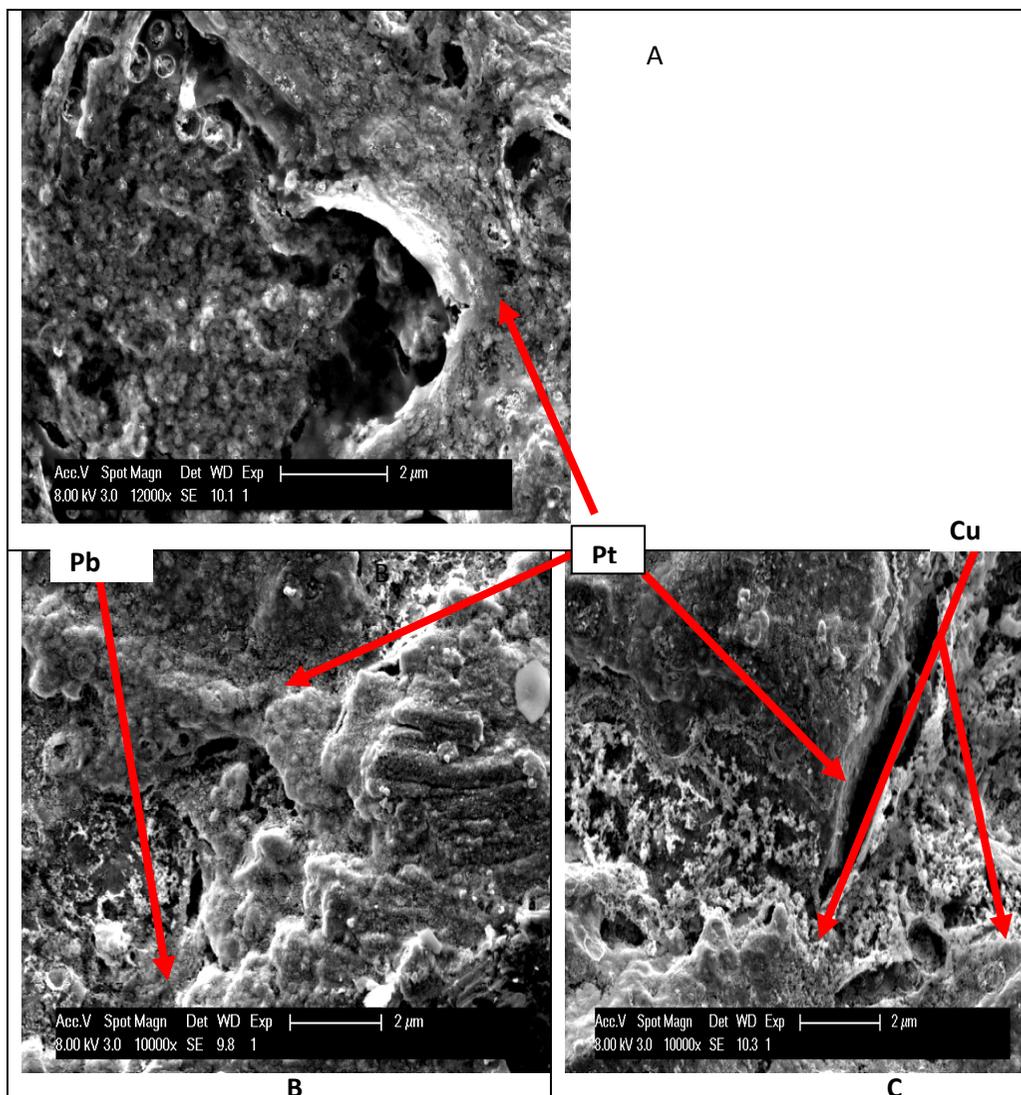


Figure 1 : *Microphotos of the prepared electrodes: (A) platinum (Pt), (B) platinum modified by lead adatoms (Pt-Pb), (C) platinum modified with copper adatoms (Pt-Cu)*

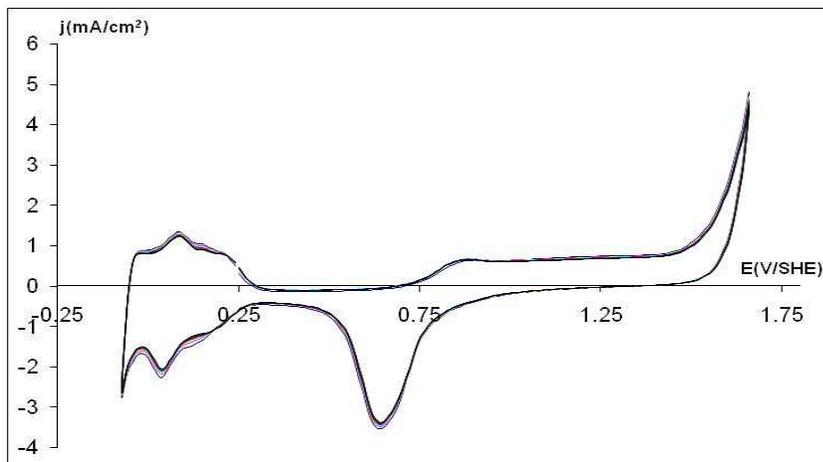


Figure 2 : Voltammogram of the platinum electrode in HClO_4 1M at 100mV/s, $T = 25^\circ\text{C}$, WE : Pt, CE : platinum wire, RE : standard hydrogen electrode

The measurements realized at 20mV/s in the potential domain located between -0,09 and 0,34V/SHE led to figure 3. In that *Figure*, the hydrogen atoms adsorption and desorption peaks are clearly present. That result indicates that the platinum electrode prepared by the thermal procedure led to a polycrystalline structure. The integration of the anodic and cathodic part of the voltammogram of *Figure 3* after the double layer correction gives a charge Q_H^0 which is related to the adsorbed and desorbed hydrogen atoms. The real surface area of the electrode could be obtained by dividing the charge Q_H^0 to $210 \mu\text{C}/\text{cm}^2$ corresponding to the charge of the adsorption and desorption of a monolayer of hydrogen atoms on the platinum electrode. The real surface area of the prepared platinum electrode was found to be 6.9 cm^2 . Its specific surface area obtained by dividing the real surface area by the deposited platinum weight in contact with the electrolyte during the voltammetric investigations is about $9058,46 \text{ cm}^2/\text{g}$. The roughness factor is about 8.6 and it has been determined using the equation $r = \frac{S_r}{S_g}$ where S_r and S_g stand respectively for the actual real surface area and for the geometric surface area. That value indicated that the platinum surface is rough confirming the observations made on the microphotos. The number of the active sites of the platinum is about 9.10^{15} considering that the electricity of a monolayer of adsorbed and removal hydrogen atom is about $1.6 \times 10^{13} \mu\text{C}$.

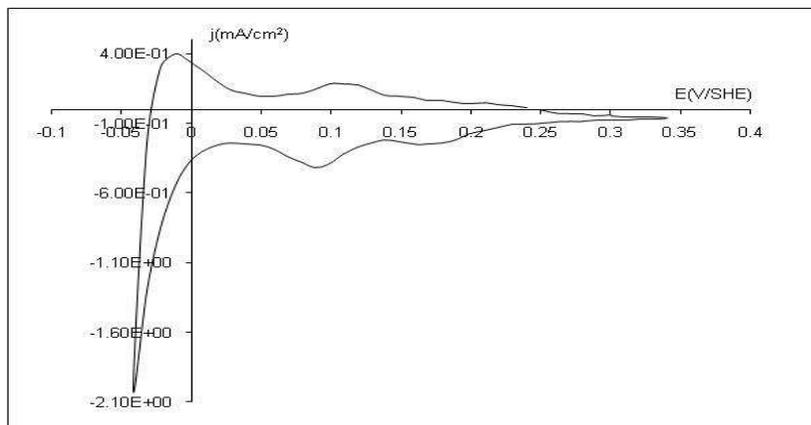


Figure 3 : Voltammogram of the platinum electrode realized between $-0,09$ and $0,34\text{V/SHE}$ in HClO_4 1M at 20 mV/s , $T= 25^\circ\text{C}$, WE: Pt, CE : Platinum wire, RE : standard hydrogen electrode

Figure 4 presents the voltammograms obtained in presence and in absence of copper ions in acidic electrolyte. The hydrogen adsorption/desorption peaks decrease in intensity in presence of the copper ions.

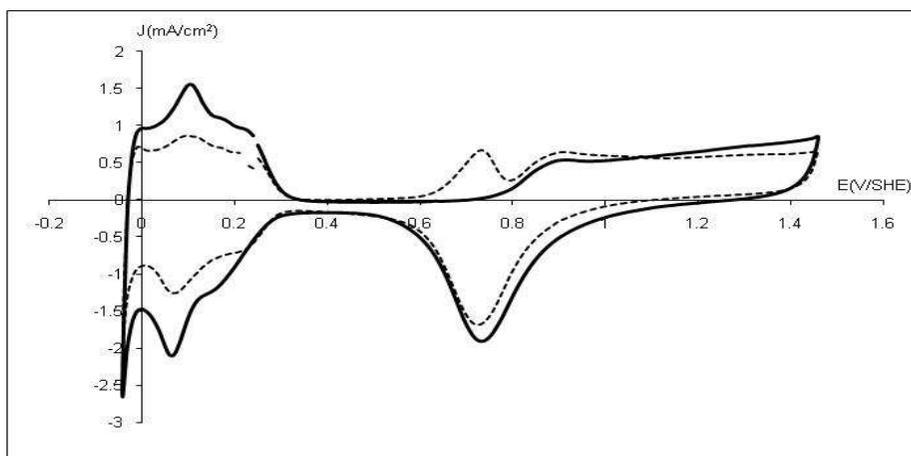


Figure 4 : Cyclic voltammograms of the platinum electrode in presence (---) and in absence (—) of copper ions in HClO_4 1M at 100 mV/s , $T= 25^\circ\text{C}$, WE : Pt, CE : platinum wire, RE : standard hydrogen electrode (SHE), copper ions concentration: 1mM

The presence of the copper adatoms on the electrode surface is indicated by the peak situated at 0.72 V/SHE corresponding to the oxidation of the adsorbed copper. The fraction of the platinum active sites occupied by the

copper adatoms obtained by using the following relation $\theta_{\text{Cu}} = \frac{(Q_{\text{H}}^0 - Q_{\text{Cu}}^0)}{Q_{\text{H}}^0}$

where $Q_{\text{Cu}}^0 = 320 \mu\text{C}$ is about 0.78. In fact, the decrease of the charge related to the adsorption and desorption of the hydrogen atoms is due to the presence of a monolayer of copper adatoms that is formed on the electrode surface.

Figure 5 presents the voltammograms obtained in presence and in absence of lead ions. The change in the voltammogram of the platinum electrode modified by lead adatoms is almost similar to that observed with the platinum modified by copper adatoms. The peak current density of the adsorbed and desorbed hydrogen atoms on the platinum electrode decreases as lead is adsorbed on the electrode surface. The fraction of the platinum electrode active sites occupied by lead adatoms is about 0.71 after calculation. A monolayer of lead adatoms occupies 71% of the active sites of the platinum electrode.

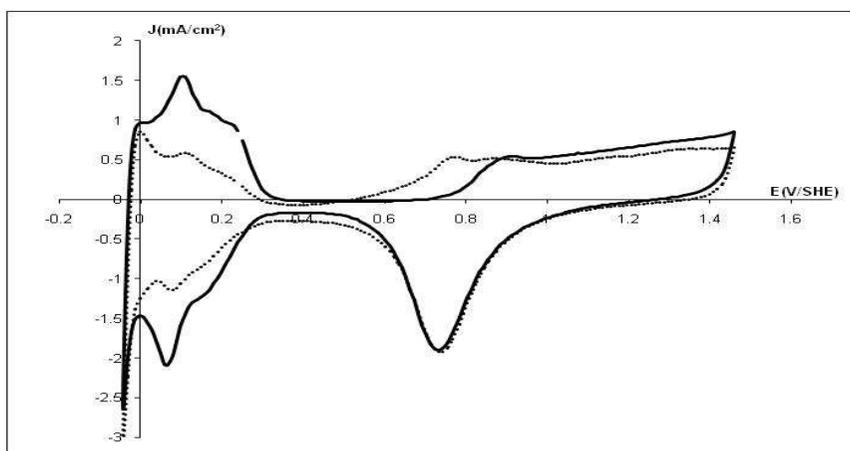


Figure 5: Cyclic voltammograms of the platinum in presence (.....) and in absence (—) of lead ions in HClO_4 1M at 100 mV/s, $T = 25^\circ\text{C}$, WE : Pt, CE : platinum wire, RE : standard hydrogen electrode (SHE), lead ions concentration: 1mM

III.3. Oxidation of the formaldehyde on the pure and modified platinum electrodes

Figure 6 presents the voltammograms realized on the pure platinum electrode in presence of 1mM of formaldehyde. In the forward potential scan, one observes three peaks at 0.87V, 1.17V and 1.41V. In the backward of the potential scan, only one anodic peak is observed at 0.76V. These peaks are

characteristic of the anodic oxidation of formaldehyde on the platinum electrode. One observes a high decrease of the hydrogen atoms adsorption and desorption current density. The onset of the potential of the first anodic peak during the forward potential scan is 0.59V. In the backward of the potential scan, the platinum oxide reduction peak is completely absent. The anodic peaks located at 0.87V, 1.17V 1.41V appear in the domain of the formation of the platinum oxide and that at 0.76V appears after the platinum oxide reduction potential. That result indicates that the formaldehyde oxidation is catalyzed by the platinum oxide in the forward potential scan and by metallic platinum in the backward of the potential scan after the totally reduced platinum oxide. In the same investigation, several cycles were successively made and it appears that an increase of the first anodic peak current density is observed until the 7th cycle and then it decreases. In fact, after several successive cycles, more intermediates resulted from the formaldehyde oxidation such as carbon monoxide (CO) was produced and since they are chemisorbed on the electrode surface, they deactivated the electrode active sites and so led to the decrease of the formaldehyde oxidation peak intensity.

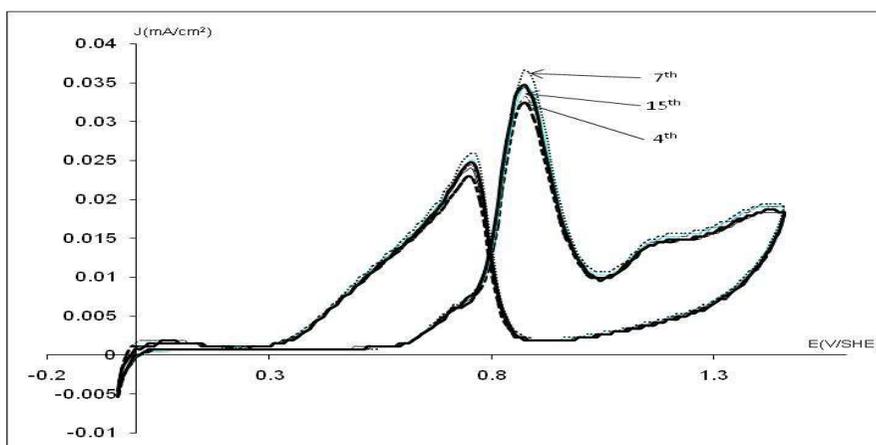


Figure 6 : Cyclic voltammograms realized during the oxidation of formaldehyde on the platinum electrode in HClO_4 1M for several potential cycles, $v=100$ mV/s, $T= 25^\circ\text{C}$, WE : Pt, CE : platinum wire, RE : standard hydrogen electrode (SHE), formaldehyde concentration: 1mM

In Figure 7, the voltammograms recorded in an electrolyte containing 1 mM of formaldehyde on pure platinum and on the platinum modified by copper adatoms were shown.

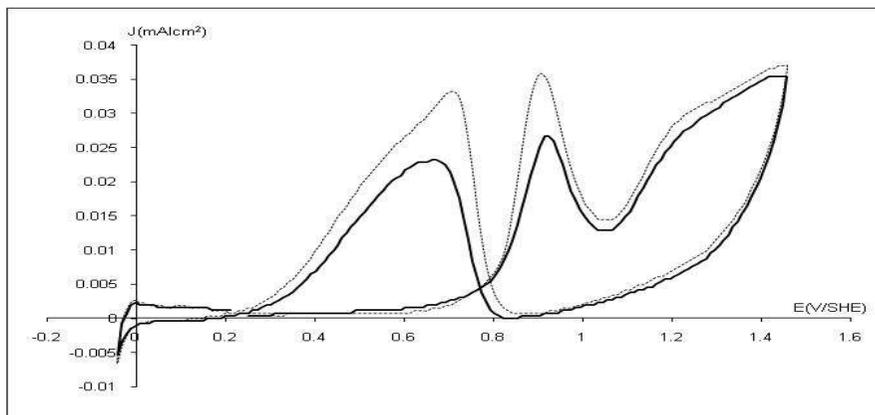


Figure 7: Cyclic voltammograms realized during the oxidation of formaldehyde on pure platinum (.....) and on platinum electrode modified by copper adatoms (—). Supporting electrolyte: HClO_4 1M, $v=100$ mV/s, $T= 25^\circ\text{C}$, WE : prepared electrode, CE : platinum wire, RE : standard hydrogen electrode (SHE), formaldehyde concentration: 1mM

The voltammograms present the same feature. The onset of the formaldehyde oxidation potential is almost the same i.e. 0.66V on both the pure platinum and on the copper adatoms modified platinum electrodes. A decrease of the peak current intensity about 25% is observed on the copper adatoms modified electrode comparatively to that obtained on the pure platinum electrode. For high values of potential, adatoms of copper seem not to influence the platinum behaviour towards the formaldehyde oxidation. This result indicate that modifying the platinum electrode with copper adatoms with a coverage of $\theta_{\text{Cu}}=78\%$ does not improve the electrocatalytic properties of the platinum electrodes for the formaldehyde oxidation.

In fact, according to the obtained result, copper adatoms seem to be inactive for formaldehyde oxidation and its adsorption on the platinum surface reduces the number of the platinum active sites that participate in the organic compound oxidation. During the oxidation process, detachment of the copper adatoms from the electrode surface occurs and so, the oxidation of the formaldehyde take place directly on the platinum surface explaining the same onset potential of the formaldehyde oxidation observed on pure platinum electrode and copper adatoms modified platinum electrodes.

Figure 8 presents the voltammograms realized during the oxidation of formaldehyde on lead adatoms modified platinum electrode and on pure platinum. The significant change between the two voltammograms is that a new formaldehyde oxidation peak appears at 0.64V. The onset potential of that oxidation process is 0.37V.

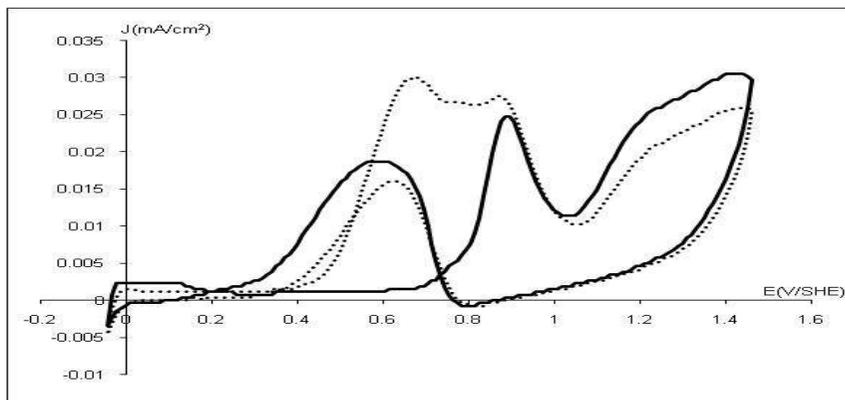


Figure 8 : Cyclic voltammograms realized during the oxidation of formaldehyde on pure platinum (—) and on platinum electrode modified by lead adatoms (.....). Supporting electrolyte: HClO_4 1M, $v=100$ mV/s, $T= 25^\circ\text{C}$, WE : prepared electrode, CE : platinum wire, RE : standard hydrogen electrode (SHE), formaldehyde concentration: 1mM

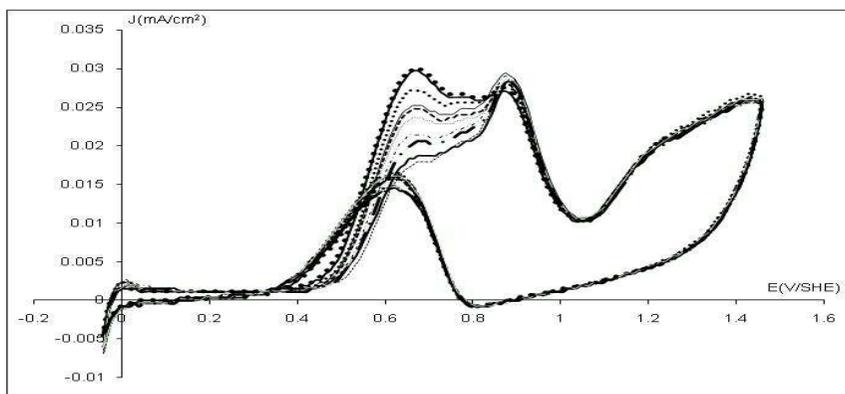


Figure 9 : Cyclic voltammograms realized during the oxidation of formaldehyde on platinum electrode modified by lead adatoms for several potential cycles. Supporting electrolyte: HClO_4 1M, $v=100$ mV/s, $T= 25^\circ\text{C}$, WE : prepared electrode, CE : platinum wire, RE : standard hydrogen electrode (SHE), formaldehyde concentration: 1mM

Varying the number of the potential cycles (Figure 9), no change of the height of the peaks located at 0.87V, 1.20V, 1.40V in the positive direction and that at 0.60V in the negative direction was observed. As the number of the cycles increases the peak located at 0.64V decreases in height and the onset of the formaldehyde oxidation potential shift to higher value.

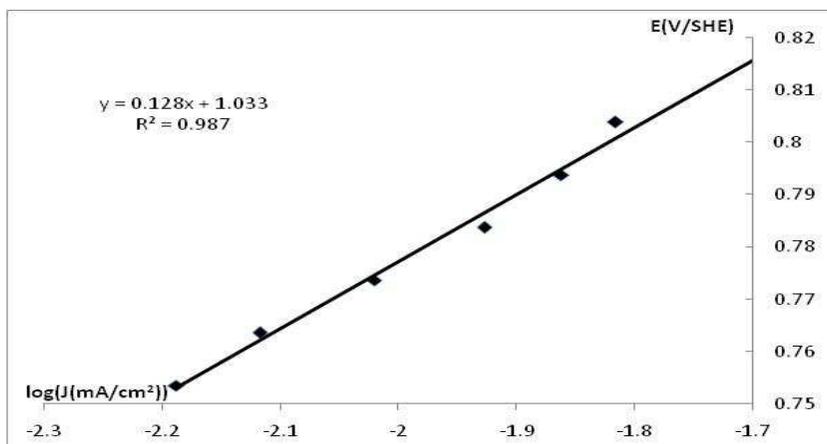
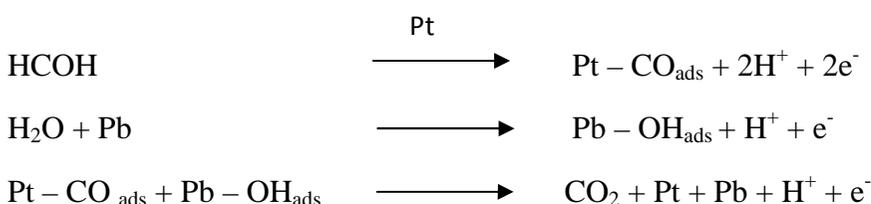


Figure 10 : Curve $E=f(\log j)$ realized the oxidation of formaldehyde on pure platinum

The oxidation of formaldehyde was made on the three types of electrode prepared in that work at a scan rate of 5mV/s. On the ascending part of the first anodic peak, the curve $E=f(\log j)$ (Figure 10) obtained with the pure platinum electrode led to a Tafel slope of 128.1 mV/dec. Those of the lead adatoms and copper adatoms modified platinum electrodes are 196.8mV/dec and 164.0 mV/dec respectively. The Tafel slopes determined in that work are very high and could be characteristic of the complex reaction that occurs on the electrodes during the formaldehyde oxidation [24].

The oxidation of formaldehyde on the platinum electrode led to several anodic peaks located in different potential domain. Hence, the formaldehyde oxidation is catalyzed by metallic platinum or by the platinum oxide. Those oxidation peaks are also observed on the modified platinum electrode by metallic adatoms during formaldehyde oxidation. The determination of the Tafel slope on the ascending part of the first anodic peak has shown high values (>128mV/dec) for all the electrodes indicating that the formaldehyde oxidation process that occurs on those electrodes is complex. On the platinum electrode modified by the adatoms of copper, the onset of formaldehyde oxidation potential is found to be almost the same as that of pure platinum and the voltammograms present the same peaks as that observed on pure platinum. In fact, the presence of the copper adatoms on the platinum electrode does not improve significantly the electrocatalytic behaviour of the platinum electrode for formaldehyde oxidation. That is possibly due to a detachment of copper adatoms from the platinum surface during formaldehyde oxidation. Hence, the adsorbability strength of copper on platinum is low according to result mentioned in literature [25]. It is

desorbed by formaldehyde and/or its intermediates during the oxidation process whence the absence of activation of platinum with copper adatoms. On the platinum electrodes modified by lead adatoms (Pt-Pb), formaldehyde oxidation starts at 0,4V i.e. almost 260 mV lower than that observed on pure platinum and on copper adatoms modified platinum electrode (Pt-Cu). The current density is high on Pt-Pb than on Pt. Those results indicate that lead adatoms improve considerably the electrocatalytic properties of platinum electrode for formaldehyde oxidation. That contributes in decreasing the oxidation potential of formaldehyde. That improvement of the platinum behaviour for formaldehyde oxidation could be explained by a bifunctional behaviour of the electrode described as follow :



Indeed, the contribution of lead adatoms to the decrease of formaldehyde oxidation potential results in the fact that they facilitate the departure of the carbon monoxide from the electrode surface by producing carbon dioxide. The mechanism proposed above to explain it, is made of several steps. One step in which a dissociative adsorption of formaldehyde occurs preferentially on the platinum active sites. That leads to the formation of carbon monoxide which is highly adsorbed on the electrode surface. A second step in which a discharge of water molecule occurs preferentially on lead adatoms is followed by the adsorption of hydroxyl radicals on the active sites of the lead adatoms. In a last step, the adsorbed species i.e. carbon monoxide and the hydroxyl radicals react between them to produce CO₂. The release of CO₂ from the electrode surface allows the lead adatoms modified platinum active sites to be free and to favor the oxidation of the other molecules of formaldehyde present in the electrolytic solution.

IV. CONCLUSION

The investigations made in that work have revealed that the platinum electrodes prepared thermally present a rough and porous surface. The electrochemical modification of thoses electrodes by copper and lead adatoms is characterized by the presence of clusters of those metals over the electrode surface. The voltammetric technique used to characterize the platinum electrode before and after its modification by adatoms allowed to

determine the platinum electrode roughness factor (8.6). The fractions of the platinum active sites covered by the adatoms of copper (78%) and by the adatoms of lead (71%). The oxidation of formaldehyde on the modified platinum electrode and on the unmodified platinum electrode is very complex. On the pure platinum, after some cycles, formaldehyde oxidation led to platinum surface deactivation by the carbon monoxide. The low adsorbability strength of copper adatoms on the platinum electrode does not allow its electrocatalytic performance improvement. But, the use of adatoms of lead led to satisfactorily results. Indeed, the hydroxyl radicals resulting from water dissociation facilitate the departure of the adsorbed carbon monoxide in the form of CO₂ from the active sites of the platinum electrode. Lead adatoms have considerably improved the electrocatalytic performance of the platinum electrode for formaldehyde oxidation.

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